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Surfactant-induced mesomorphic structures in flexible polymers

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Abstract. – During the last two years, mesomorphic structures for polyelectrolytes with ionically bound surfactants have been reported. This has now been extended to the case of hydrogen bonding. For poly (4-vinyl pyridine)-pentadecyl phenol (P4VP-(PDP)$_x$), the long period L_p of the lamellar structure is found to *decrease* as a function of x, in complete contrast to polyelectrolyte systems. Scaling arguments predict that the x-dependence of the long period is entirely due to the reduction in the thickness of the polymer layer and satisfies $L_p \propto x^{-1}$, as observed experimentally. Polyelectrolyte-surfactant complexes, on the other hand, are always locally fully complexed due to cooperative complexation with a corresponding x-independent long period.

In recent years, surfactant-induced mesomorphic structures have been achieved with semi-rigid polymers [1]-[3] and with more flexible polyelectrolytes [4]-[7]. Antonietti *et al.* studied poly(styrene sulfonate) and poly(acrylic acid) complexes with alkyl trimethyl ammonium salt surfactants. Mesomorphic layered structures were obtained with alternating highly ionic and non-polar alkyl layers. The layer thickness depends on the length of the alkyl chain of the surfactant and also a cylindrical morphology with the ionic backbone chains embedded in a continuous alkyl matrix was observed. Similar layered structures have been found by us using atactic poly(vinyl pyridine) and dodecyl benzene sulfonic acid (DBSA) [7]. Here, proton transfer between the surfactant and the polymer takes place, again leading to a strong polyelectrolyte-surfactant complex. In all these cases the presence of charges may lead to multiplets, thus promoting layering of the polymer backbones. Our next step was to remove the requirement of *bound* ionic charges along the polymer backbone and to extend the concept also to other than polyelectrolytes. To this end, surfactants that form transition metal coordination complexes with the aminic nitrogens of poly(vinyl pyridine) were selected and shown to induce mesomorphic structures at high loading of the surfactant; zinc dodecyl benzene sulfonate

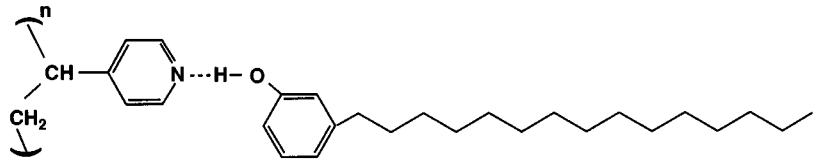

Fig. 1. – Hydrogen bond between P4VP and PDP.

($Zn(DBS)_2$) in this particular case [8]. Note that a polyelectrolyte is not obtained because there are no covalently *bound* charges along the polymer backbone, although there are still ionic charges *complexed* to the polymer due to the ionic zinc sulfonate salt of the surfactant.

To avoid these complications, to study the weak-bonding limit and to extend the principle of molecular self-assembly to a more general class of flexible polymer-surfactant systems, very recently hydrogen bonding between polymer and surfactant was considered [9]. Hydrogen bonds have interactions strengths of the order of 1–10 kcal mol^{-1}, which implies that at room temperatures hydrogen bonds are constantly broken and reformed. To investigate these weakly bonded systems, poly(4-vinyl pyridine) (P4VP) was selected as the flexible polymer and 3-pentadecyl phenol (PDP) as the surfactant. In this case hydrogen bonding between the hydroxyl group of PDP and the basic aminic nitrogen of the pyridine group takes place. Figure 1 presents such a hydrogen bond. Figure 2 presents the long period of the lamellar structure obtained experimentally by small-angle X-ray scattering for P4VP-$(PDP)_x$ systems as a function of x, the fraction of surfactant molecules per P4VP repeat unit. The observed decrease with x is in complete contrast to the behaviour of the polyelectrolyte-surfactant complex system P4VP-$(DBSA)_x$, as well as the P4VP-$(Zn(DBS)_2)_x$ coordination complex system, presented in the inset of fig. 2 [6], [7].

To address the x-dependence of the long period L_p, the lamellar structures of polymer-surfactant complexes will be modelled as a layer, containing the polymers, to which the

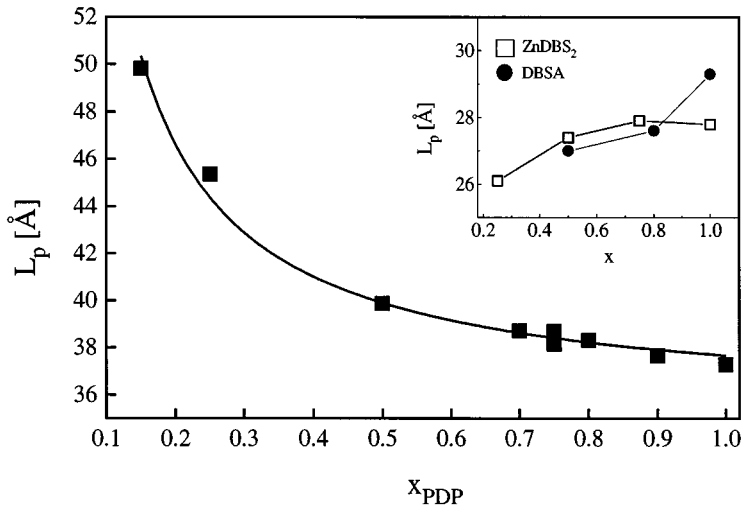

Fig. 2. – Long period of P4VP-$(PDP)_x$ as a function of x at room temperature. The solid line represents $1/x$ fit. Inset: long period of P4VP-$(DBSA)_x$ and P4VP-$(Zn(DBS)_2)_x$ at room temperature.

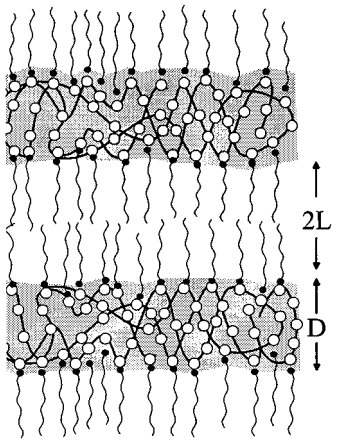

Fig. 3. – Polymer-surfactant model ($x = 0.25$).

surfactant side chains are attached. The situation resembles a polymer brush with dimensional parameters determined by a balance between 1) the free energy of the polymer confinement in a two-dimensional layer of thickness D, 2) the interaction energy between the polymer layer and the surfactant brush and 3) the free energy of stretching the surfactant molecules up to a length L. Figure 3 illustrates the lamellar model with $L_p = L + 2D$.

The free energy due to the confinement of the polymers inside a layer with thickness D with a diffuse interface of thickness Δ can simply be incorporated in the familiar Helfand expression [10] for the interfacial free energy

$$F_{\text{int}} = 2\gamma A \cong \frac{A\chi^{1/2}}{a^2} kT\,, \tag{1}$$

where χ represents the unfavourable interaction between the surfactant tail and polymer layer, a is the segment size and A the interface area. To see this [11], we note that the loss of conformational entropy due to the confinement of the polymer molecule occurs inside the interface of thickness $\Delta \cong a\chi^{-1/2}$ and amounts to kT per loop. This loop contains on the average $g \propto \chi^{-1}$ segments and, consequently, there will be of the order of $A\Delta/ga^3$ loops for the slab considered, bringing us back to the right-hand side of eq. (1). The observation that the loss of conformational entropy is located in the interface is based on the ideal random walk behaviour beyond a distance of the order of the persistence length from the interface. It sets an important limit on the applicability to the present situation, as we will see.

Finally, the free energy of stretching F_{str} will be considered. Since stretching of the homopolymer chains only increases the conformational free energy without reducing the interfacial free energy, it seems reasonable to assume that only the surfactant side chains are stretched. In this respect, it is also important to realize that due to the dynamic nature of the complexation process, the polymer chain can easily explore all conformations satisfying the confinement constraint. The free energy due to stretching of the side chains is given by [12]

$$F_{\text{str}} \cong \sigma N a \frac{AD}{Na^3} \frac{3L^2}{2na^2} kT\,. \tag{2}$$

Here the first factor σNa represents the number of surfactant molecules per chain of N segments, the second term represents the number of chains per layer and finally, the last

two terms represent the free energy of stretching a side chain of n segments to a length L. Here we assume uniform stretching of all side chains and absence of interpenetration between the surfactant brushes. In reality, the chain ends are distributed throughout the layer and some interpenetration will occur [13]-[17]. Taking this into account would change numerical factors. However, in this analysis most numerical factors have or will be dropped since their presence only suggests unwarranted accuracy. As a further simplification, all segments (main chain and side chain) have been assumed to be of equal size.

To make the problem self-consistent, we observe that the volume $2AL$ of the side chains attached to the polymer layer equals the number of side chains times the volume per side chain, hence

$$2AL = \sigma N a \frac{AD}{Na^3} n a^3 \longrightarrow L = \frac{\sigma}{2} a n D \,. \tag{3}$$

From this we finally obtain for the total free energy per unit volume

$$\frac{1}{A(2L+D)} \frac{\Delta F}{kT} \cong \frac{1}{1+\sigma a n} \Big(\frac{\chi^{1/2}}{a^2 D} + \frac{\sigma^3 n D^2}{4a^2} \Big) \,. \tag{4}$$

Minimizing this expression as a function of D leads to

$$\frac{1}{2} D^3 \sigma^3 n = \chi^{1/2} \,. \tag{5}$$

This equation demonstrates that

$$D \cong \sigma^{-1} \chi^{1/6} n^{-1/3} \,, \tag{6}$$

$$2L \cong a \chi^{1/6} n^{2/3} \,, \tag{7}$$

$$L_p \cong \chi^{1/6} [\sigma^{-1} n^{-1/3} + a n^{2/3}] \,. \tag{8}$$

Hence, the long period decreases inversely proportional to σ, as observed experimentally, and the decrease is entirely due to the reduction of the polymer layer thickness D.

In our model the segments of the polymers and the surfactant molecules have the same size and σ can at most be $2/a$. For $\sigma = 2/a$, the assumption of a lamellar morphology automatically implies full stretching of the surfactant molecules and hence, $D = a$, $L = na$. This is clearly not a realistic situation. For these high amounts of complexation, which as discussed by Fredrickson [18] can easily be achieved in solution, different structures such as bottle-brushes with more space for the long-tail surfactant molecules may appear. In the case of P4VP-$(PDP)_x$, the methyl groups of the surfactant tail are considerably smaller than the vinylpyridine groups. Hence, even at values of x close to 1, *i.e.* full complexation, the effective σ that corresponds to it is considerably smaller than $1/a$. Still, for increased complexation the polymer layer thickness D will become comparable to the persistence length of the polymer or even smaller, in which case the analysis given is not fully correct any more.

Polyelectrolyte-surfactant complexes are characterized by the fact that the complexation takes place in a highly cooperative manner (zipper mechanism) [5], [19], [20]. As a consequence, the systems contain primarily chain fragments that are almost fully complexed and which subsequently aggregate to form microphase separated domains. In such a case an x-dependence of the long period is not expected. The slight increase observed experimentally might be due to the diminishing role of the domain boundaries. Similar arguments hold for the P4VP$(Zn(DBS)_2)_x$ system.

The systems considered have many features in common with block copolymer systems including those obtained by blending homopolymer with block copolymer (in our case corresponding to an excess of surfactant), where new morphologies continue to be found [21], [22]. Other related systems, also recently considered, are polymers attached to fluid membranes [23]. The experiments and theory described above are only the beginning of this new field of surfactant-induced mesomorphic structures in flexible polymers. By systematically varying the surfactant tail length and surfactant concentration, a wide variety of different morphologies can in principle be realized. Moreover, new interesting self-assembled systems may be designed using the principle of hydrogen bonding for surfactants equipped with additional functionalities.

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